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DRAWINGS ATTACHED

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(19)

(54) IMPROVEMENTS IN OR RELATING TO CRUCIBLE FREE SINTERING OR MELTING OF GLASS, GLASS-CERAMIC, CERAMIC OR REFRACTORY MATERIALS

(71) We, AMERICAN OPTICAL CORPORATION, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of 14 Mechanic Street, Southbridge, State of Massachusetts, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to crucible free sintering or melting of glass, glass-ceramic, ceramic or refractory materials. The term crucible free refers to the use of the unmelted portion of a body of precursor material as a receptacle for the melted portion thereof. It includes such use in low or zero gravity environments where the whole body eventually becomes melted.

High melting ceramic compounds are usually prepared by one or a combination of several methods. In one method, batch material as a powder or pelletized, is placed in a crucible which is more refractory (has a higher melting temperature) than the melt to be prepared. The filled crucible is then heated to the fusion temperature of the melt, for example, in a combustion furnace, a high temperature electric furnace, an induction furnace, or the like. Regardless of the type of crucible used, contamination of the melt by material of the crucible cannot be avoided. In another method, batch material is heated in a solar furnace or in the focus of an intense beam of light. In this method the sample is either placed in a crucible or on a refractory plate, and in some instances may be supported on a refractory pin. Where the material is placed on the refractory plate or refractory pin, contamination of the melt by the crucible material may be avoided to some extent. The solar furnace, however, depends upon the presence of the sun as a heat source. The intense light source, when used, involves a very difficult furnace control, and the amount of heat generated is limited by the efficiency of the light source.

In still another method, batch material is heated to sintering or melting temperature with plasma torches. The heat is applied either locally to the surface of the batch or by heating the crucible which contains the batch. Plasma torches, as well, as gas-fired furnaces, including combustion type furnaces, require a gas as a heat carrier. Therefore, melts under vacuum or arbitrarily chosen atmospheres cannot be performed at higher temperatures. Still another method is to locally heat batch material to sintering or melting temperature in vacuum by means of an electron or ion beam.

In all the presently used methods, a number of disadvantages are present. If crucibles are used, the applied heat necessary to melt the high-melting refractory materials is usually sufficient to cause a reaction between the crucible material and the batch constituents, thereby causing contamination of the melt of the material to be sintered. Induction heating requires the use of crucibles, therefore, contamination cannot be avoided. Furthermore induction furnaces are limited in maximum temperature by the melting or vaporization of the conductor which is used to transform electromagnetic energy into heat. Solar surfaces, since they depend upon the presence of the sun, have limited applicability. As noted above, plasma torches and gas-fired furnaces are limited to a combustion-type atmosphere. Electron or ion beam heating results in selective volatization of batch components, and furthermore, requires the application of high vacuum in which the sample is to be heated or placed.

According to the present invention, there is provided a method of crucible free sintering

or melting of a glass, glass-ceramic, ceramic or refractory material, comprising forming a mass of a precursor of such a material of a sufficient quantity to form a body of said material precursor which is to be melted or sintered and applying at least one beam from a CO_2 laser directly to the body for a sufficient period of time to sinter or melt at least a surface layer of said mass of material precursor.

The term directly includes passing the laser beam through a window which is not in contact with the body, the window being substantially transparent at the wavelength of the laser beam.

A specific embodiment of the invention will now be described by way of example and with reference to the accompanying drawing which is a side elevation, generally schematic view of one form of a furnace for providing an atmospheric controlled sintering or melting of refractory material by a laser light.

In general, the embodiment utilizes a beam of infrared light from a CO_2 gas laser as a source of radiant heat for surface heating a depth of powdered or pelletized refractory material. The infrared light beam, produced by the CO_2 laser, may be focused by optical means on the surface of the sample, to provide point or area heating. Due to the high absorption of most ceramic batch material at a wavelength of 10.6 microns (106,000 Angstrom units), the infrared radiation energy is transformed into heat within a thin layer of the surface of the batch. The body of the batch may be heated subsequently by conduction and radiation from the surface. The amount of heat generated in the surface may be readily controlled either by monitoring the output energy of the laser or by varying the energy density of the laser beam at the place of interaction with the material. Such control may be readily achieved, for example, by using slightly convergent or divergent laser beams and/or changing the distance between the optical system of the laser and the sample. Control may, also, be achieved by changing the angle of convergence or divergence by infrared optical means. Size of the area of the batch surface in relation to the generated infrared beam or beams, determines the number of beams necessary to effectively cover the area to be sintered or melted. The batch may be rotated or vibrated in such a manner that uniform heat distribution is achieved throughout the surface, and into the body of the batch. Furthermore, it is possible to move the laser beam or beams continuously over the surface of the batch for applying the beam to a larger area.

In the following examples, batch material was supported by a thick layer of its own composition, thus avoiding introduction of impurities from supporting refractory plates or crucibles. All of the samples of these examples were prepared in air in a closed chamber.

Example 1.

A pellet, having a size approximately of 0.5 cm. cube, of a barium crown glass batch was fused into a glass within 25 seconds by applying an infrared beam onto the pellet. The CO_2 laser used for the experiment has only 25 watts output power.

Example 2.

A mixture of powder having a composition by weight of 70% Al_2O_3, 20% SiO_2, and 10% BaO, after being subjected to a laser beam resulted in a fused, solid containing principally Al_2O_3, small amounts of a second unidentified crystalline phase, and a glass phase acting as a binder between the crystals. The powder was subjected to the CO_2 laser of Example 1.

Example 3.

A sample of powder having a composition by weight of 70% Al_2O_3, 20% SiO_2, 10% MgO was exposed to the infrared beam from a CO_2 laser for approximately 30 seconds. The result was a strong sintered body composed of Al_2O_3 crystals, magnesium-aluminium-spinel, and an identified amorphous phase.

Example 4.

Powder having a composition of approximately 100% Al_2O_3 was sintered into a strong body within approximately 40 seconds when the powder was subjected to an infrared CO_2 laser beam.

Example 5.

About 100% ZrO_2 powder was sintered into a complex crystalline, strong body, within 60 seconds when the powder was subjected to the infrared beam from a CO_2 laser.

The device shown in the single figure of the drawing is a preferred chamber construction for melting according to the embodiment of the invention. It is comprised of a base member 10, having a removable, dome-shaped cover 12, which is sealable to the base 10 forming a hermetic seal so that the interior of the cover 12 may be subjected to high vacuum or a controlled atmosphere as desired. An outlet line 14 controlled by a valve 16 communicates with a pump 18 for evacuating the volume under the cover 12. A shield or hood 20 prevents direct passage of gas from the volume into the line 14. An inlet line 22 controlled by a valve 24 provides means for introducing gas into the cover 12 as desired. A shield or hood 26 over the inlet line 22 diffuses the flow of incoming gas into the interior. A turntable 30 controlled by a shaft 32 provides a support for a sample 34 resting on the table. The table may be mounted on a trunnion 36 with appropriate bearings

for easy turning. A motor and gearing arrangement, not shown, rotates the turntable where desired. Hermetically sealed in the cover 12 is an infrared transmitting window 40 on the one side and an infrared transmitting window 42 on the opposite side for introducing the infrared rays from a laser. A laser beam from a CO_2 laser, not shown, impinges on a mirror 44 at the one side and the beam is reflected through the window 40 onto the surface of the sample. A beam on the opposite side reflects a laser beam through the window 42 and onto the sample. As illustrated, the beams reflected from mirrors 44 and 46 are shown as being essentially collimated; however, depending upon the particular energy density requirements of the specific application, either or both of the beams shown might be either diverging or converging. Obviously, one or more windows may be placed in the cover 12 for admitting one or more laser beams. Furthermore, the mirrors may be changed to provide coverage of the surface of the sample on the table as may be desired for the particular sintering or melt. Also, where desired, the sample may be preliminarily heated with an induction coil and additionally heated by means of the laser beams. It will be appreciated that the melt is supported on the material itself, thereby foregoing the need of other types of support for the refractory material melted. In the above examples the controlled atmosphere was air. Other atmospheres, for example, ones inert with respect to the material precursor may be used as can a reduced pressure atmosphere. For example, in preparing nitrites a nitrogen atmosphere can be used .

It will also be appreciated that the embodiment of the invention has application in low or substantially zero gravity environments such as one might find in an earth-orbiting satellite. Crystallization of a piece of glass takes place only if nuclei are present. Many glasses form such nuclei during cooling just because of their chemical composition (homogeneous nucleation). In these cases, zero gravity would not affect devitrification. However, there are glasses in which nuclei are introduced from external sources (heterogeneous nucleation). The most important of these sources is crucible attack by the glass melt. Glasses may be formed from compounds with even a high rate of crystal growth if they do not exhibit homogeneous (or "intrinsic") nucleation and if they are prepared under conditions which eliminate heterogeneous nucleation. Containerless melting in low or zero gravity environments and in vacuum is such a process.

Surface tension casting, modified by inertia and electric field casting methods, offers the possibility of producing optical elements with fire polished surfaces directly from the melt. Lenses and mirror blanks, usually of rotational symmetry, but in many cases with aspheric surfaces, are presently made by grinding and polishing. Although it is possible to prepare rather smooth surfaces by these methods, there are still irregularities left on the order of 1—10 nm. Fire-polished surfaces are smoother by about one order of magnitude. In most optical instruments, the degree of smoothness reached by mechanical polishing is satisfactory. However, there are some special instruments which could be improved in performance if the traces of surface roughness caused by mechanical polishing could be eliminated. Besides selecting small areas out of float glass, there is at present no way to achieve such high quality surfaces under conventional conditions. So-called "precision molding" is applied to produce, e.g., condenser lenses with fire-polished surfaces. In that case, metal or ceramic molds are used to shape the viscous glass at high temperature under various pressures. The reproducibility of the lens' curvature and the elimination of chill wrinkles present real problems. The solution is to shape the lens without having the hot glass in contact with the mold. Mold-free forming would be limited only by the availability of force field (inertia and electric) and heat sources in an orbiting laboratory.

A preferred glass for low or zero gravity melting is as follows:

Batch Composition		Oxide Composition	
Constituent	Grams	Constituent	Wt. %
SiO_2	32,899.60	SiO_2	68.52
Na_2CO_3	6,033.60	Na_2O	7.35
K_2CO_3	5,016.00	K_2O	11.13
KNO_3	4,147.20		
$Ba(NO_3)_2$	3,998.40	BaO	4.90
Sb_2O_3	489.60	Sb_2O_3	1.02
$Al(OH)_3$	1,123.20	Al_2O_3	1.53
ZnO	734.40	ZnO	1.53
Li_2CO_3	1,209.60	Li_2O	1.02
Nd_2O_3	1,440.00	Nd_2O_3	3.00
	57,081.60		100.00

The following table sets forth other possible uses for the present invention:

Process	*Product*
1. Melt column of Batch consisting of high purity raw materials into glass rods.	Laser glass billets (Nd- and Er-doped) of 10—20 liters volume. Dimensions of rods: approximately 8—15 cm diameter; 100—200 cm long.
2. Melt tablets of glass powder mixed with semi-conductive, particularly photoconductive particles in vacuum, nitrogen and air.	Light filters with integral transmission depending on intensity and/or spectral distribution of incident light. Volume of individual samples approximately 100 cm^3.
3. Melt tablets of a low melting glass containing coarse particles of high melting glass.	Christiansen filter. Volume of individual samples approximately 100 cm^3.
4. Remelt optical glass blanks in electric field and/or under rotation.	Lenses and mirror blanks with firepolished surface and non-spherical curves.
5. Remelt blanks of glasses sensitive to thermal convection.	Homogeneous low refractive index-low dispersion glass in large pieces. Volume of individual blanks approximately 20 liters.
6. Melt foam glass batches.	Structural material to be used in and around a space laboratory.

An especially interesting application of the present invention is its use as a hot stage in a metallographic or crystallographic microscope.

In a low or zero gravity environment the ceramic or refractory material is present in a quantity sufficient to form a body or mass which can be acted upon by the CO_2 laser. Upon application of heat and formation of a liquid, restricting mold configurations are absent, because of surface tension the liqiuid naturally forms a sphere. In such an environment all other shapes, as noted above, are controlled by restricting mold configurations, rotational (centrifugal) forces and electrical field casting methods.

WHAT WE CLAIM IS:—

1. A method of crucible free sintering or melting of a glass, glass-ceramic, ceramic or refractory material, comprising forming a mass of a precursor of such a material of a sufficient quantity to form a body of said material precursor which is to be melted or sintered and applying at least one beam from a CO_2 laser directly to the body for a sufficient period of time to sinter or melt at least a surface layer of said mass of material precursor.

2. A method as claimed in claim 1, wherein the beam from the CO_2 laser has a wavelength of 106,000 Angstrom units.

3. A method as claimed in claim 1 or claim 2, wherein a predetermined atmosphere is maintained around said mass of material precursor during said application of said laser beam thereon.

4. A method as claimed in any one of the preceding claims, wherein said mass of material precursor is enclosed in a confined enclosure having at least one window for passing a laser beam onto said mass of material precursor.

5. A method as claimed in claim 4, wherein said confined enclosure is hermetically sealed, and maintaining said mass of material precursor therein in a predetermined atmosphere.

6. A method as claimed in any one of the preceding claims, in which the melting occurs in a low or zero gravity environment.

7. A method as claimed in claim 1, wherein two or more laser beams are applied to the surface of said mass of material precursor.

8. A method as claimed in any one of the preceding claims, wherein at least one laser beam is reflected from a mirror onto said mass of material precursor.

9. A method as claimed in any one of the preceding claims, wherein said at least one laser beam is divergent prior to applying the same onto the surface of said mass of material precursor.

10. A method as claimed in any one of claims 1 to 8, wherein said at least one laser beam is convergent prior to applying the same onto the surface of said mass of material precursor.

11. A method as claimed in any one of the preceding claims, wherein said melting is undertaken in an atmosphere which is inert with respect to the material precursor.

12. A method as claimed in any one of claims 1 to 10, wherein said melting is undertaken in a vacuum.

13. A method substantially as hereinbefore described with reference to and as illustrated in the accompanying drawing.

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1307263 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*